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# TECHNICAL REPORT

**WHITE OAK LABORATORY**

PREDICTION OF MOISTURE ABSORPTION IN THE 5"54 HIGRAG DISCARDING ROTATING BAND FOR VARIOUS CLIMATIC ENVIRONMENTS

BY
J.M. Augl                                    3 FEBRUARY 1977

NAVAL SURFACE WEAPONS CENTER
WHITE OAK LABORATORY
SILVER SPRING, MARYLAND 20910

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
The equilibrium sorptions of moisture in filled and unfilled Nylon 612 were determined as a function of relative humidity. Average diffusion coefficients for these materials were determined between room temperature and 100°C. These data were used to calculate the rate of moisture uptake in the 5"/54 HIFRAG Discarding Rotating Band for various climatic environments and laboratory exposure conditions. Simple guidelines are given which

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will enable the weapons engineer to predict the rate of moisture uptake for various other environments. The method outlined can also be easily extended to other similar problems.

The use of protective coatings as moisture barriers was also considered. It was concluded that organic coatings are not very beneficial though a Teflon coating of 1 mil may lead to a 38% reduction in the rate of moisture uptake. An excellent moisture barrier was obtained with a 1-mil thick copper coating that was chemically deposited on the surface of the Nylon.

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PREDICTION OF MOISTURE ABSORPTION IN THE 5"54 HIFRAG DISCARDING
ROTATING BAND FOR VARIOUS CLIMATIC ENVIRONMENTS

This work is part of a technical evaluation of the 5"54
Nylon HIFRAG Rotating Band developed at the NSWC/DL.

During the technical evaluation phase of the Rotating Band
failures were observed when reduced charges were used in firing
tests with moisture loaded bands.  Some of the bands either failed
to discard by fracturing or slipped off as a whole piece.  Such a
failure can cause the shell to fall short of the target.

This work was designed to investigate the absorption of mois-
ture in unfilled and filled Nylon 612, and to predict the amount
of moisture a Rotating Band would absorb as a function of time under
various laboratory or climatic exposure conditions.

This work was sponsored during the FY 1976, by the Naval Sea
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Amendment A.

J. DIXON
By Direction

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INTRODUCTION


The work described in this report is part of the technical
evaluations program of the 5"54 Nylon 612 HIFRAG Discarding Rotating
Band which is presently underway at the Naval Surface Weapons
Center (Dahlgren Laboratory).

During the firing tests with reduced charges, it was observed
that bands, previously soaked in hot water, failed to discard
properly.  They either slipped off as a whole piece from the shell
instead of fracturing, or remained undamaged on the shell causing
a reduced range.  It seemed that approximately two percent of mois-
ture content in these bands led to failures.  It therefore was
necessary to investigate which natural storage environments would
lead to such a high moisture content, and, how long it would take
to reach equilibrium with its surrounding.

As will be shown, in most environments, where the average
relative humidity is lower than 85%, the moisture level in the
Rotating band should not exceed 2 percent.

The analytic approach taken here was kept simple enough that
it can be carried out with ordinary desk calculators, though the
details were originally worked out with a more involved computer
program where real weather data of temperature and humidity were
supplied in three hourly time steps.

Background

The 5"54 Nylon HIFRAG Rotating Band is a component of the
HIFRAG Mod 1 Projectile.  This rotating band was designed to discard
after the projectile leaves the gun barrel thus reducing its drag.
The band must be strong enough to withstand certain criteria of
rough handling (defined by a drop test); on the other hand, it should
fracture and discard when leaving the gun.  The band material must
have enough shear strength to effectively transmit the spin to the
projectile and it must meet certain temperature requirements dictated
by the loading and firing conditions.

Nylon 612 met all these mechanical properties. However, during an extended test firing program, it was observed that those bands that had been soaked in hot water for some time showed a considerable number of failures when fired with reduced charges. Some of the bands did not break up, as dry Nylon bands did, but remained either fastened to the projectile or discarded as a whole piece. Both of these behaviors are undesirable because it may result in a decreased range.

A program was initiated to study possible failure mechanisms more thoroughly in order to understand and predict the problems that may be encountered in service.

We do not intend to discuss in great detail the various failure mechanisms that have been proposed and how they may be eliminated. Suffice it here to mention that the properties of Nylon 612 change drastically when moisture plasticizes the material. For instance, the elongation at break increases from about 10% to 300% (reaching a maximum at 2% moisture concentration). The Izod impact strength increases from .75 to 1.3 ft-lb (between 2-3% of moisture content). The glass transition temperature of Nylon 612 (as shown in this work) may be reduced from 70°C down to 0°C depending on the amount of moisture absorbed. Changes have been made in the original design of the band geometry to increase the fracture sensitivity. Also, modifications in the material were proposed with the general philosophy that fillers in the Nylon 612 or change in its molecular weight might alter the materials properties enough to overcome these problems.

Also, an investigation was made of possible storage environments, which indicate that a water submersion test is an extremely unrealistic environmental test. Normal ship storage environments are in the average not more than 80°F and 50-82% RH.

The purpose of this investigation was to predict what kind of moisture levels one can expect these bands would attain in various environments and how long it would take for the band to reach equilibrium with the surrounding humidity.

Five materials were of immediate interest: unfilled Nylon 612, and Nylon 612 filled with 10% each of talcum, glass, mineral and a special "alloy" (of proprietary nature). The diffusion coefficients measured in this work are average diffusion coefficients, and, due to the urgency of the problem, no attempt was made to investigate the finer details of the concentration dependence of the diffusion coefficients, because it was not expected that by neglecting these fine points the results would change significantly, particularly when the relative humidities of interest are below 85% RH.

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## Experimental

### A. Materials

The following materials were used for determining diffusion coefficients and equilibrium concentrations: Nylon 612 and Nylon 612 filled with 10% glass, with 10% talcum, with 10% glass alloy, and with 10% mineral. These materials were supplied by DeBell and Richardson who produced the discarding rotating bands and carried out other mechanical measurements on these materials.

### B. Measurement of Diffusion Coefficients

1. Equilibrium Concentrations. To determine the equilibrium concentrations, the polymer pellets were well pressed at 150°C between hot platens of a hydraulic press to give a film which was then dried for 48 hours at 125°C and equilibrated at various levels of relative humidity. The equilibrium concentration was defined as the concentration when the weight increase versus time curve leveled out, which generally occurred within a few days. The percent weight gain after two weeks was designated the equilibrium concentration.

2. Fractional Weight Increase. Round plates, 5 cm in diameter and 0.23 cm thickness, were exposed to various temperatures and relative humidities and their fractional weight increase $M_t(\%)/M_\infty(\%)$ was plotted versus square root of time, where $M_t$ is the percent weight increase after the time (t) and $M_\infty$ is the equilibrium value.

The samples were put into a sample holder and placed in a wide-mouth crew cup container (23.5 cm high, 11.5 cm diameter). Various salt solutions (2 cm high, with undissolved solute) served to keep the relative humidity constant. The containers were closed and submerged into water baths at different constant temperatures.

### C. Teflon Coating of Nylon Discs

The Nylon discs where surface etched with light sand paper, quickly cleaned with methylethyl ketone, spray-coated with 958-207 Teflon-S finish, and heat treated for ten minutes at 325°F to give a 1 mil thick coating.

## DISCUSSION AND RESULTS

### A. Geometry of Rotating Band

The dimensions of the HIFRAG 5"/54 Rotating Band were obtained by measuring a production specimen and are shown in Figure 1.

For the purpose of calculating the moisture absorption in the entire band, the band geometry was divided into 6 sections. The average thickness, the square of half the thickness, and the fractional volume of each section are given in Table 1.

### B. Diffusion Coefficient

The average diffusion coefficients of unfilled Nylon 612 and filled Nylon 612 specimens were determined from the slopes of the sorption curves ($M_t/M_\infty$ versus $t^{\frac{1}{2}}$) and were calculated as indicated in reference [1] p. 248.

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{\frac{1}{2}}} \left(\frac{Dt}{\ell^2}\right)^{\frac{1}{2}}$$

where $M_t$ = amount of moisture absorbed at time t
  $M_\infty$ = equilibrium concentration
  $D$ = diffusion coefficient
  $\ell$ = thickness of slab

The values of $M_\infty$ were determined on film specimens and are shown in Figure 2 as a function of the surrounding relative humidity. The measured diffusion coefficients and their temperature dependences are shown in the Arrhenius plot (Figure 3) and the values are listed in Table 2.

### C. Calcuation of the Moisture Absorption in the Rotating Band

The transient absorption in a hollow cylinder with b as the outer radius and a as the inner radius, and with the concentrations of the diffusant equal on both sides of the cylinder wall and zero inside the wall material can be obtained by solving Fick's second diffusion equation (1) with the corresponding boundary conditions

$$C_t = D(C_{xx} + C_{yy} + C_{zz}) \tag{1}$$

where the C is concentration, D is the diffusion coefficient and the subscripts t and xx, yy and zz refer to the first and second derivatives of time and space coordinates respectively.

The solution is given by equation (2) [1]

$$\frac{M_t}{M_\infty} = 1 - \frac{4}{b^2-a^2} \sum_{n=1}^{\infty} \frac{J_o(a\alpha_n) - J_o(b\alpha_n)}{\alpha_n^2 \{J_o(a\alpha_n) + J_o(b\alpha_n)\}} e^{-D\alpha_n^2 t} \tag{2}$$

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Table 1

Dimensions of Rotating Band used in the Calculation of the
Moisture Absorption

| Section # | Average Thickness (cm) | $h^2$ (cm$^2$) | Fractional Volume |
|-----------|------------------------|----------------|-------------------|
| 1 | 1.47 | .5402 | .3384 |
| 2 | 1.23 | .3782 | .2831 |
| 3 | .35 | .0306 | .0537 |
| 4 | .67 | .1122 | .1542 |
| 5 | .45 | .0506 | .1036 |
| 6 | .30 | .0225 | .0806 |

## Table 2

Diffusion Coefficients and Equilibrium Concentrations
of Moisture in Filled and Unfilled Nylon 612

| Filler | Measured at ($^{\circ}$C) | (RH) % | Equilibrium Concentration (%) | Diffusion Coefficient ($cm^2$/sec) |
|---|---|---|---|---|
| None | 30 | 30 | .49 | 6.01 E-9 |
| None | 30 | 80 | 1.54 | 6.25 E-9 |
| None | 100 | 100 | 3.103 | 2.34 E-7 |
| None | 75 | 100 | – | 8.5 E-8 |
| 10% Mineral | 100 | 100 | 2.764 | 2.20 E-7 |
| 10% Mineral | 30 | 80 | 1.635 | 1.50 E-9 |
| 10% Mineral | 30 | 100 | 3.035 | – |
| 10% Talcum | 100 | 100 | 2.776 | 2.12 E-7 |
| 10% Talcum | 30 | 80 | 1.624 | 1.44 E-9 |
| 10% Talcum | 30 | 100 | 2.994 | – |
| 10% Glass | 100 | 100 | 3.061 | 2.16 E-7 |
| 10% Glass | 30 | 80 | 1.730 | 1.40 E-9 |
| 10% Glass | 30 | 100 | 3.078 | – |
| 10% Alloy | 100 | 100 | 2.720 | 1.96 E-7 |
| 10% Alloy | 30 | 80 | 1.448 | 2.61 E-9 |
| 10% Alloy | 30 | 100 | 3.075 | – |
| Teflon Coated (1 mil) | 30 | 80 | – | 3.87 E-9 |

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where $J_O$ is the Bessel function of the first kind of zero order, $\alpha_n$'s are the roots of $J_O(a\alpha_n) = 0$.

If the ratio of b to a approaches 1, the solution is that of a flat infinite slab for which the solution is given by Equation (3)

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi 2} \sum_{n=o}^{\infty} \frac{1}{(2n+1)^2} e^{-D(2n+1)^2 \pi^2 t/h^2} \qquad (3)$$

where h is half of the thickness of the slab. There is very little difference in the absorption of a flat sheet and a hollow cylinder with b/a<10 (reference [1] page 77). We, therefore, used the solution (3) of a flat sheet, which is given graphically in [1] and is shown in Figure 4. The diagram shows the internal moisture distribution ($Dt/h^2$ curves) in dimensionless coordinates as a function of time. $X/\ell=0$ represents the midplan of the slab.

Integration of these $Dt/h^2$ curves leads to a diagram indicated by Figure 5 which is a master curve of sorption for all materials with Fickean diffusion characteristics.

Since the HIFRAG Rotating Band has a complex geometry, we made the following simplifications. The moisture absorption of the rotating band was calculated piecewise in six sections (indicated in Figure 1). The slightly conical ring sections were calculated as if they had a cylindrical shape with an average thickness as given in Table 1. (The error caused by this simplification is negligible).

The error caused by not including the edge effect of the flat end of the Rotating band is of a factor of 1.08. This error is almost cancelled by not including the edge effect on measuring the diffusion coefficient on the disc specimens which leads to an error of a factor of 1.03 in the same direction. Thus, the difference in these errors are within the experimental uncertainty.

The total moisture absorption was then considered as the sum of the moisture absorptions in each section multiplied by their fractional volumes.

Thus, if the diffusion coefficient of moisture in Nylon 612 is known as a function of temperature, and if the equilibrium concentrations of moisture are also known as a function of the surrounding partial pressure of moisture (or relative humidity), then one can immediately calculate the moisture uptake of the Rotating Band (at constant temperature and constant humidity).

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1. J. Crank, The Mathematics of Diffusion, Oxford (1956).

An example of such a calculation is given in Table 3 where the $Dt/h^2$ values for the Nylon 612 Rotating Band sections, the percent of the sorption equilibrium values and the total moisture uptake are listed for exposure times from 10 to 4000 hours at a temperature of 71°C (160°F) and 100% RH. Obviously, the thin sections (3 and 6) of the band will be saturated long before the thicker sections.

### D. Calculations of the Moisture Absorption in an Environment with Variable Temperature and Variable Humidity

In order to calculate the moisture uptake in a cylinder (or slab) exposed to some real outdoor environment where temperature and humidity change continuously, one can solve the problem in two ways:

a. by using pseudo constant boundary conditions. This procedure requires a reasonable averaging procedure that will correspond to realistic outdoor conditions.

b. by solving the diffusion equation with a finite difference approach, such, that the variable boundary conditions (RH) and the variable diffusion coefficient (due to temperature) are supplied in successive small time intervals. For instance, weather data (temperature and moisture) are available for many areas in 3 hourly time intervals. These magnetic tapes can be read directly by the computer.

Obviously, the second procedure requires a high-speed computer since tens of thousands of time steps may be required in the calculation. For procedure a, the following assumptions are made: the thickness of the wall is large enough that daily humidity fluctuation will lead to only negligible relative weight changes; the changes in rate of absorption and its corresponding weight uptake due to daily or seasonal temperature fluctuations can be neglected for the time-span of interest; and, the determined yearly averages will also be the same in the future. For procedure b, the assumption is made that a 3 hourly time step is small compared to the total time of interest.

Procedure b is less sensitive to the slab thickness; it requires a computer while procedure a can be carried out with a desk calculator and is, therefore, more useful for engineering estimates. Again, it is assumed that past yearly average temperatures and humidities will not change in the near future.

We have calculated systems by using both procedure a and b. For all practical purposes, they give the same results. Suffice it, therefore, to discuss here only procedure a because of its practical engineering value. (Procedure b will be discussed in detail in a forthcoming TR).

Table 3  Percent Moisture Uptake as a Function of Time in the HIFRAG Rotating Band
(at 71°C; D = 6.3 x E-8 cm2/sec, 100% RH)a

| $Dt/h^2$ for Section | t=10 | t=50 | t=100 | t=200 | t=350 | t=500 | t=1000 | t=2000 | t=4000 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.20 E-3 | 2.09 E-2 | 4.20 E-2 | 8.40 E-2 | 1.47 E-1 | 2.09 E-1 | .420 | .839 | 1.68 |
| 2 | 6.00 E-3 | 2.98 E-2 | 6.00 E-2 | 1.20 E-1 | 2.10 E-1 | 2.99 E-1 | .600 | 1.199 | 2.39 |
| 3 | 7.42 E-2 | 3.69 E-1 | 7.42 E-1 | 1.48 | 2.59 | 3.69 | 7.412 | 14.82 | 29.6 |
| 4 | 2.02 E-2 | 1.01 E-1 | 2.02 E-1 | 4.05 E-1 | 7.08 E-1 | 1.01 | 2.021 | 4.04 | 8.08 |
| 5 | 4.49 E-2 | 2.23 E-1 | 4.49 E-1 | 8.97 E-1 | 1.57 | 2.23 | 4.482 | 8.96 | 17.9 |
| 6 | 1.01 E-1 | 5.02 E-1 | 1.01 | 2.02 | 3.53 | 5.02 | 10.08 | 20.1 | 40.3 |
| Percent of equilibrium concentration | 14.36 | 31.6 | 42.8 | 55.2 | 65.8 | 72.4 | 85.8 | 96.7 | 100 |
| Percent, total moisture uptake in 100% RH | .445 | .980 | 1.327 | 1.711 | 2.04 | 2.24 | 2.66 | 3.00 | 3.103 |

a) The time t is given in hours

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If we neglect the very thin surface layer, where daily fluctuations in temperature and humidity cause moisture concentration changes in the polymer, one can imagine that the interior moisture distribution in a slab could also be obtained if the band were exposed to some constant temperature and relative humidity as boundary conditions over the same time period.  Such average temperature and humidity we call kinetic average temperature ($T_{kav}$) and kinetic average relative humidity ($RH_{kav}$).

The question, therefore, is how to determine such $T_{kav}$ and $RH_{kav}$.

From the fact that the diffusion coefficient is exponentially dependent on temperature as indicated by (4)

$$D = D_O \, e^{-\frac{E}{RT}} \tag{4}$$

it is apparent that the arithmetic average temperature ($T_{av}$) should not be used for the calculation but rather the temperature $T_{kav}$ that corresponds to the average diffusion coefficient.  ($D_O$ in (4) is a constant, E = activation energy of diffusion, obtained from the Arrhenius plot of log D vs. $1/T$, T is the absolute temperature in $^O$K and R = ideal gas constant).

The average diffusion coefficient $D_{kav}$ (daily, monthly or yearly) is obtained by converting the temperature curves (daily, monthly or yearly) into diffusion coefficient curves using a linear interpolation of the straight lines in Figure 3 (log D vs. $1/T$).  The $D_{kav}$ value was obtained from the diffusion coefficient curves by numerical integration (Simpson's rule) and averaging. $D_{kav}$ was then converted back by the inverse operation to give the corresponding temperature $T_{kav}$.  The larger the temperature fluctuations are, the larger is the positive deviation of $T_{kav}$ from the average temperature $T_{av}$ (see Section E).

For the kinetic average surface concentration boundary condition we can not simply use the average relative humidity $RH_{av}$ giving an average surface concentration because a) the diffusion rates are highest at the peak temperatures where the relative humidity is lowest, leading to desorption, b) the concentration gradient may be high at low temperatures leading to absorption, c) the equilibrium concentration is usually not linearly related to the relative humidity of the environment (see Figure 2).  The problem of determining $RH_{kav}$ is, therefore,  more complicated than for $T_{kav}$.  However, we can state that the temperature dependence of the diffusion coefficient can be made temperature independent by an equivalent dilation or contraction in time.  In other words the same amount of material can diffuse through a unit surface area when the temperature is high for a short time or low for a long time. This is quantitatively described by equations (4) and (5),

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$$q = -D \frac{dc}{dx} \tag{5}$$

where q is the flux of material per unit time and unit surface area, and dc/dx is the concentration gradient.

Keeping the temperature constant at $T_{kav}$ over this dilated-contracted time, and letting the concentration vary (using the data of Figure 2) corresponding to the environmental changes in relative humidity, we can now integrate over the variable concentration curve and obtain the corresponding $RH_{kav}$.

We have devised a computer program that can give $T_{kav}$ and $RH_{kav}$ values from recorded weather data, from the known temperature dependent diffusion coefficient and from the known RH dependent equilibrium moisture concentrations. Since details of this program are of secondary importance here, only rules of thumb will be given in the following section of how much $T_{kav}$ and $RH_{kav}$ deviate from $T_{av}$ and $RH_{av}$ for various climatic areas on earth. Assuming that $T_{kav}$ and $RH_{kav}$ have been evaluated, the determination of the overall moisture uptake and the internal moisture distribution can now proceed as described under C.

### E.  Eight Categories of Climatic Conditions

Guidelines for realistic considerations of climatic conditions in research, development, test and evaluation have been published by the Army under Army Regulation AR 70-38, July 1969. This report divided the earth's climatic conditions into eight climatic categories:

    Category 1, wet-warm
    Category 2, wet-hot
    Category 3, humid-hot coastal desert
    Catetory 4, hot-dry
    Category 5, intermediate hot-dry
    Category 6, intermediate cold
    Category 7, cold
    Category 8, extreme cold

A reproduction of the world map indicating these climatic areas from AR 70-38 is shown in Figure 6. For all categories, a representative daily temperature and humidity cycle is given for "operational" and "storage and transit" conditions. We have calculated the $D_{kav}$ and $RH_{kav}$ of Nylon 612 for all eight categories for the operational and storage conditions (Table 4) and compared these values with the $D_{av}$ values corresponding to the average temperature ($T_{av}$) and the average relative humidity $RH_{av}$. This gives practical correction factors, which are given in Table 4. The way these correction factors should be used is to look up the yearly temperature and humidity averages of a particular environment, then determine to which climatic category it will belong. Then the

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Table 4. Average and Kinetic Average Temperature and Humidity Conditions and Kinetic Average Diffusion Coefficients of Nylon 612 for the Eight Climatic Categories[a]

| Cat | | \| Time of day | | | | | | | | | $T_{av}$ | $T_{kav}$ | $(F_T)$ Factor | $RH_{av}$ | $RH_{kav}$ | $(F_{RH})$ Factor | $D_{kav}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 3 | 6 | 9 | 12 | 15 | 18 | 21 | 24 | | | | | | | |
| 1 | RH | 100 | 100 | 100 | 95 | 95 | 95 | 100 | 100 | 100 | | | | 97.5 | 97.5 | 1.00 | 3.93 E-9 |
| | oF | nearly constant at 75° | | | | | | | | | 75. | 75. | 1.00 | | | | |
| | RH | 100 | 100 | 95 | 95 | 95 | 95 | 100 | 100 | 100 | | | | 97.5 | 97.5 | 1.00 | 4.73 E-9 |
| | oF | nearly constant at 80° | | | | | | | | | 80 | 80 | 1.00 | | | | |
| 2 | RH | 80 | 79 | 78 | 82 | 75 | 74 | 82 | 95 | 82 | | | | 88.5 | 90.5 | 1.023 | 5.98 E-9 |
| | oF | 79 | 80 | 84 | 87 | 94 | 95 | 90 | 83 | 80 | 85.7 | 86 | 1.007 | | | | |
| | RH | 75 | 80 | 84 | 74 | 30 | 10 | 35 | 59 | 75 | | | | 55.9 | 37.5 | .672 | 2.42 E-8 |
| | oF | 98 | 94 | 91 | 117 | 150 | 160 | 142 | 105 | 98 | 119.6 | 129 | 1.076 | | | | |
| 3 | RH | 82 | 90 | 79 | 66 | 63 | 64 | 68 | 75 | 82 | | | | 73.4 | 73.1 | .997 | 7.80 E-9 |
| | oF | 89 | 86 | 88 | 97 | 100 | 100 | 96 | 92 | 89 | 93.5 | 94 | 1.004 | | | | |
| | RH | 75 | 80 | 84 | 74 | 30 | 10 | 35 | 59 | 75 | | | | 55.9 | 37.5 | .672 | 2.42 E-8 |
| | oF | 98 | 94 | 91 | 117 | 150 | 160 | 142 | 105 | 98 | 119.6 | 129 | 1.076 | | | | |
| 4 | RH | 15 | 17 | 19 | 12 | 7 | 5 | 7 | 10 | 15 | | | | 11.5 | 9.7 | .846 | 1.24 E-8 |
| | oF | 95 | 94 | 91 | 101 | 115 | 125 | 116 | 105 | 95 | 105.2 | 107 | 1.019 | | | | |
| | RH | 46 | 50 | 30 | 8 | 2 | 14 | 33 | 41 | 28 | | | | 28 | 15.1 | .541 | 2.42 E-8 |
| | oF | 98 | 94 | 91 | 117 | 150 | 160 | 142 | 105 | 98 | 119.6 | 129 | 1.076 | | | | |
| 5 | RH | 72 | 85 | 83 | 63 | 28 | 23 | 36 | 54 | 72 | | | | 55.5 | 46.9 | .845 | 7.04 E-9 |
| | oF | 75 | 71 | 73 | 90 | 106 | 109 | 96 | 83 | 75 | 87.9 | 91 | 1.035 | | | | |
| | RH | 41 | 46 | 50 | 30 | 10 | 5 | 14 | 33 | 41 | | | | 28.6 | 16.3 | .572 | 1.71 E-8 |
| | oF | 75 | 71 | 73 | 117 | 135 | 145 | 135 | 100 | 75 | 106.4 | 117.3 | 1.103 | | | | |
| 6 | RH | close to 100 | | | | | | | | | | | | 100 | 100 | 1.00 | 7.00 E-11 |
| | oF | -24 | -25 | -15 | -15 | -5 | -6 | -13 | -19 | -24 | -16.5 | -14.5 | .911 | | | | |
| | RH | close to 100 | | | | | | | | | | | | 100 | 100 | 1.00 | 4.45 E-11 |
| | oF | -29 | -30 | -28 | -28 | -19 | -13 | -20 | -26 | -29 | -24.4 | -23 | .961 | | | | |
| 7 | RH | close to 100 | | | | | | | | | | | | 100 | 100 | 1.00 | 1.44 E-11 |
| | oF | -49 | -50 | -45 | -45 | -35 | -35 | -39 | -45 | -49 | -43.5 | -42.5 | .977 | | | | |
| | RH | close to 100 | | | | | | | | | | | | 100 | 100 | 1.00 | 1.44 E-11 |
| | oF | -49 | -50 | -45 | -45 | -35 | -35 | -39 | -45 | -49 | -43.5 | -42.5 | .977 | | | | |
| 8 | RH | close to 100 | | | | | | | | | | | | 100 | 100 | 1.00 | 3.24 E-12 |
| | oF | -69 | -70 | -69 | -69 | -61 | -60 | -63 | -66 | -69 | -66 | -65.5 | .992 | | | | |
| | RH | close to 100 | | | | | | | | | | | | 100 | 100 | 1.00 | 3.24 E-12 |
| | oF | -69 | -70 | -70 | -69 | -61 | -60 | -63 | -66 | -69 | -66 | -65.5 | .992 | | | | |

a) The first two lines in each category are the storage and the following 2 lines are the operational conditions (from AR-70-38). The $D_{kav}$ refer to unfilled Nylon 612 (calculated from the experimentally determined diffusion coefficients).

averages are multiplied by the corresponding $F_T$ and $F_{RH}$ factors. The $T_{kav}$ and $RH_{kav}$ values thus obtained are used as pseudo constant temperature and humidity conditions. Additional corrective terms may be required if the material is exposed also to direct sun radiation because of the temperature increase in the black Rotating Band. The difference in temperature between the ambient air and the black surface may be $40^O$ to $50^O$F.

Over a period of several weeks, continuous temperature recordings were taken on flat specimens exposed to and shielded from direct sun radiation. The differences in temperature between the shielded and unprotected specimens depended on the time of day, on angle of incident radiation on sky conditions (clear, hazy, cloudy) and on wind conditions. The integral effects of various exposure conditions may be simplified by the following approximation.

Let us assume the following exposure conditions: open air on a clear, sunny day (cs), open air on a clear, sunny but windy day (cw), open air on a hot, hazy day (hh), open air on a cloudy, rainy day (cr), protected from open sky radiation (p). The sample will be exposed for different, fractional numbers of days, $f_{cs}$, $f_{cw}$, $f_{hh}$, $f_{cr}$, and $f_p$ to these conditions. Then the average kinetic diffusion coefficient including sun irradiation $D_{kavr}$ is obtained from (6)

$$D_{kavr} = D_{kav} \left( f_{cs} \times 2.05 + f_{cw} \times 1.64 + f_{hh} \times 1.47 \right.$$
$$\left. + f_{cr} \times 1.14 + f_p \times 1.00 \right) \tag{6}$$

The constant values 2.05, 1.64, etc., were experimentally obtained from the outdoor exposure data. (It should be remembered that in the $D_{kav}$ values the correction factor for the climatic category is already included.) So that the whole procedure may be shown schematically by

$$\text{look up } \begin{Bmatrix} RH_{av} \\ T_{av} \end{Bmatrix} \xrightarrow[\substack{\text{climatic} \\ \text{category}}]{\text{corr. for}} \begin{Bmatrix} RH \times F_{RH} \\ T_{av} \times F_T \end{Bmatrix} \rightarrow \begin{Bmatrix} RH_{kav} \\ D_{kav} \end{Bmatrix} \xrightarrow[\text{radiation}]{\text{corr.}} \begin{Bmatrix} RH_{kav} \\ D_{kavr} \end{Bmatrix}$$

For storage conditions where only the air temperature governs the materials temperature, this reduces to the simple formula (7).

$$D_{kavr} = D_{kav} \tag{7}$$

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If the temperature fluctuations over daily and seasonal periods are small, as found aboard a ship,

$$D_{kav} = D_{av} \text{ and } RH_{kav} = RH_{av}$$

(Obviously $T_{av}$ and $RH_{av}$ are then the average temperature and humidity inside the storage room.)

Figure 7 shows the relative moisture uptake of the unfilled Nylon 612 Rotating Band for these 8 climatic categories for both operational and storage conditions.

To obtain the absolute moisture uptake, one has to know the equilibrium concentration of moisture as a function of relative humidity. (For Nylon 612 this is shown in Figure 2.) From this graph the ultimate concentration that will be reached can be determined directly by looking up the concentration corresponding to the value of $RH_{kav}$.

By combining Figure 7 and Figure 2, we are now in a position to estimate the moisture uptake (in percent) for various climatic conditions as a function of time. An example of moisture uptake for the conditions of categories 1-3 are shown on Figure 8 for the Talcum filled and unfilled Nylon 612 Rotating Band.

### F. Experimental Verification

The calculations described in section C and D may be used in two ways. First, one may calculate the percent moisture uptake (and the internal moisture distribution if so desired) as a function of time. Or, second, one may want to prepare, for testing purposes, samples with a specified moisture content (or internal distribution).

We have verified experimentally the predicted values in both ways. The moisture uptake in Rotating Bands exposed at various conditions agree very well with the predicted values.

In another experiment, it was desired to prepare for firing purposes a series of talcum-filled Rotating Bands having a uniform internal distribution of one and two percent of moisture.

From Figure 2, it can be seen that these conditions can be achieved in an environment of 55% and 90% RH, respectively. In order to achieve these equilibrium concentrations in a sufficiently short time, it was decided to expose the bands at $103^{\circ}$ and $118^{\circ}$C, respectively, in an oven where steam was introduced at atmospheric pressure. These temperatures regulate automatically the relative humidities (see Figure 9).

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The exposure times were set so that 95% of the equilibrium values should be reached.
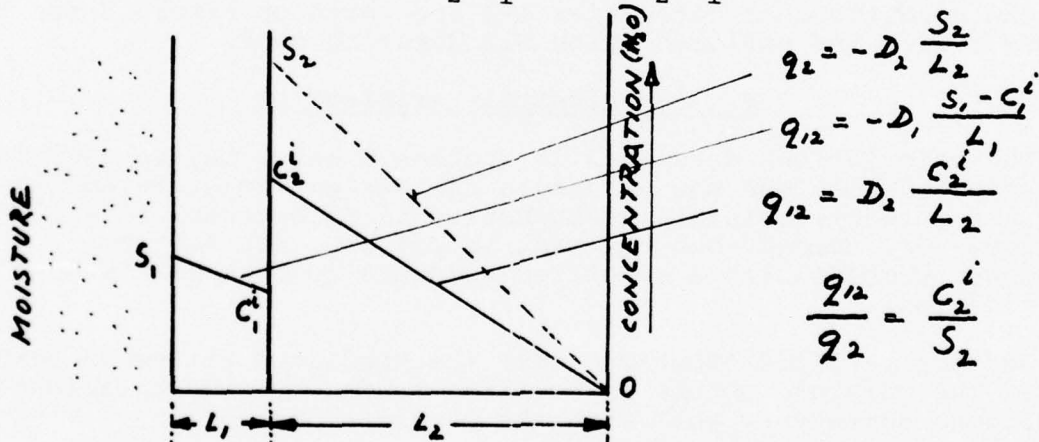
Nineteen and 8 days were calculated to be required to reach 95% of equilibrium at 103° and 118°C, respectively (see Figure 10). As can be seen from Table 5 the predictions still agree very well even for these high exposure temperatures.

## G.  Potential of Coatings to Reduce the Rate of Moisture Absorption

The question of whether one might use an organic coating as a moisture barrier is an obvious one.

A few simple arguments will demonstrate what one might expect from such an approach.

Let us consider a steady state water permeation through a slab composed of a thin coating of a substance (1) and a wall of another substance (2).  At the side of the coating, the moisture concentration is kept constant leading to a surface concentration $C_0 = S_1$ ($S_1$ = solubility of moisture in-substance (1) at a constant RH). The concentration on the surface of substance 2 is kept at zero. The concentrations on both sides of the interface (i) are given by the distribution coefficient $C_2^i / C_1^i = k = S_2 / S_1$



$$q_2 = -D_2 \frac{S_2}{L_2}$$

$$q_{12} = -D_1 \frac{S_1 - C_1^i}{L_1}$$

$$q_{12} = D_2 \frac{C_2^i}{L_2}$$

$$\frac{q_{12}}{q_2} = \frac{C_2^i}{S_2}$$

Since at the steady state the flux is the same throughout the slab, one obtains

$$D_1 \frac{S_1 - C_1^i}{L_1} = D_2 \frac{C_2^i}{L_2}$$

Table 5.   Preparation of Rotating Bands with 1 and 2 Percent Uniform Internal Moisture Distribution

| Band # | Orig. Weight (g) | Final Weight (g) | Exposure (days) | Exposure Temp (°C) | % Weight gain |
|---|---|---|---|---|---|
| 1416 | 371.0 | 374.6 | 8 | 118 | .96 |
| 1433 | 368.4 | 372.2 | 8 | 118 | 1.03 |
| 1477 | 369.0 | 372.6 | 8 | 118 | .98 |
| 1472 | 369.2 | 372.9 | 8 | 118 | 1.05 |
| 14131 | 368.1 | 371.8 | 8 | 118 | 1.00 |
| | | | | average | 1.004 |
| 1499 | 369.1 | 376.3 | 19 | 103 | 1.94 |
| 1495 | 370.5 | 377.7 | 19 | 103 | 1.95 |
| 1424 | 300.0 | 377.4 | 19 | 103 | 2.01 |
| 1413 | 368.8 | 376.0 | 19 | 103 | 1.96 |
| 1423 | 369.3 | 376.3 | 19 | 103 | 1.90 |
| | | | | average | 1.95 |

Using permeabilities $P_1 = S_1 D_1$ and $P_2 = S_2 D_2$, one obtains further

$$\frac{P_1 S_1}{S_1 L_1} - \frac{P_1 C_1^i}{S_1 L_1} = \frac{P_2 C_2^i}{S_2 L_2}$$

$$C_2^i = \frac{P_1 \; k \; S_1 \; L_1 \; S_2 \; L_2}{L_1 (P_1 S_2 L_2 + P_2 k S_1 L_1}$$

Now the reduced flux due to the coating can be calculated from the ratio

$$\frac{q_{12}}{q_2} = \frac{C_1^i}{S_2} = \frac{P_1 \; k \; S_1 \; L_2}{(P_1 \; S_2 \; L_2 + P_2 \; k \; S_1 \; L_1)}$$

$$= \frac{1}{1 + \dfrac{P_2}{P_1} \dfrac{L_1}{L_2}} \quad \text{or} \quad \frac{1}{1 + \dfrac{kD_2}{D_1} \dfrac{L_1}{L_2}} \tag{8}$$

Table 6 shows values of the reduced flux through the slab for various ratios of permeabilities and ratios of coating to substrate thicknesses. It is quite obvious that a coating with a very low permeability (about 1/1000 of that of the substrat) would be required to give a useful protection, or the thickness of the coating has to be increased considerably.

The only possible candidates that might be considered to have some effect are polymers such as teflon, polyvinylidene chloride, polyvinylidene fluoride and, perhaps, a few highly fluorinated polymer films.

Metal coating, on the other hand, would be sufficient even in very thin films to protect the Nylon from moisture.

A 1 mil thick copper film was chemically deposited on Nylon 612 samples (Frankfort Arsenal). There was no measurable moisture uptake after 72-hour water boil.

Samples were also coated with Teflon (1 mil thick). From the apparent diffusion coefficient measured on these samples, a reduction of 38 percent in the rate of moisture uptake was estimated which is probably not sufficient for all climatic conditions to give a desired projectile lifetime of 15 years.

Table 6.  Reduced Permeation of Gases through a Composite
Membrane (Film & Substrate)

| $P_2/P_1$ \\ $L_1/L_2$ | 0.001 | 0.005 | 0.01 | 0.05 | 0.1 |
|---|---|---|---|---|---|
| 1000 | .50 | .167 | .091 | .02 | .01 |
| 500 | .67 | .285 | .167 | .038 | .02 |
| 100 | .91 | .67 | .50 | .167 | .091 |
| 50 | .95 | .80 | .67 | .285 | .167 |
| 10 | .99 | .95 | .91 | .67 | .50 |
| 5 | .995 | .975 | .95 | .80 | .67 |

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## H.  Thermomechanical Behavior of Nylon 612

Samples of unfilled Nylon 612 were dissolved in formic acid for impregnation of TBA glass braids.  After removal of the solvent in vacuum at 115°C, a torsional braid analysis (TBA) was run in the temperature range between -160° to +150°C.  Figures 11 and 12 show the damping factors and relative moduli of samples that were dry, and exposed to 55 and 100% relative humidity.

A strong shift in the glass transition temperature (Tg) can be observed, which is due to the plasticizing effect of the absorbed moisture.  A shift from 70° to 0°C can be seen which may explain the strong change in elongation and impact behavior of moisture exposed samples.  A secondary transition appears at -60°C in moisture exposed braids.  This transition extends over a broad distribution of frequencies from $10^2$ to $10^5$ Hz, centered at 1000 Hz. The impact resistance (toughness) of Nylon 612 should therefore increase with absorption of water because of the ability of the $\beta$ transition to attenuate the impact stress wave.

## CONCLUSIONS AND RECOMMENDATIONS

1.  The percentage of ultimate moisture uptake of the 5"54 HIFRAG Nylon 612 Rotating Band depends on the "kinetic" average relative humidity of the storage environment.  If the average relative humidity remains below 85%, it is not expected that the Rotating Band will absorb more than 2 percent of moisture.

2.  The rate of moisture absorption depends on the kinetic average temperature and, therefore, is strongly dependent on the climatic area.  While in hot tropical zones, 95% of the equilibrium concentration may be reached between 2 and 5 years; it may take several hundred years in the arctic area.

3.  It has been shown that once the storage environment is known, one can readily estimate the moisture uptake with time.  It is particularly simple to estimate if the bands are stored aboard a ship, since the temperature fluctuations are not extreme.  But even for open air exposure with sun radiation, it is not difficult to obtain a reasonable estimate.

4.  Organic coatings such as teflon may increase the time to reach the equilibrium concentration by about 40%, depending on the coating thickness, but they do not prevent moisture absorption; and, therefore, these coatings are not of great benefit.

5.  Metallic coatings (for instance a 1 mil thick copper film, chemically deposited) give an excellent moisture barrier.

6.  Potential substitute materials for Nylon 612 should have a low affinity to moisture and still retain the good mechanical and temperature properties of Nylon 612.  As a possible candidate material, we suggest P1700 polysulfone, though it will require higher moulding temperatures.
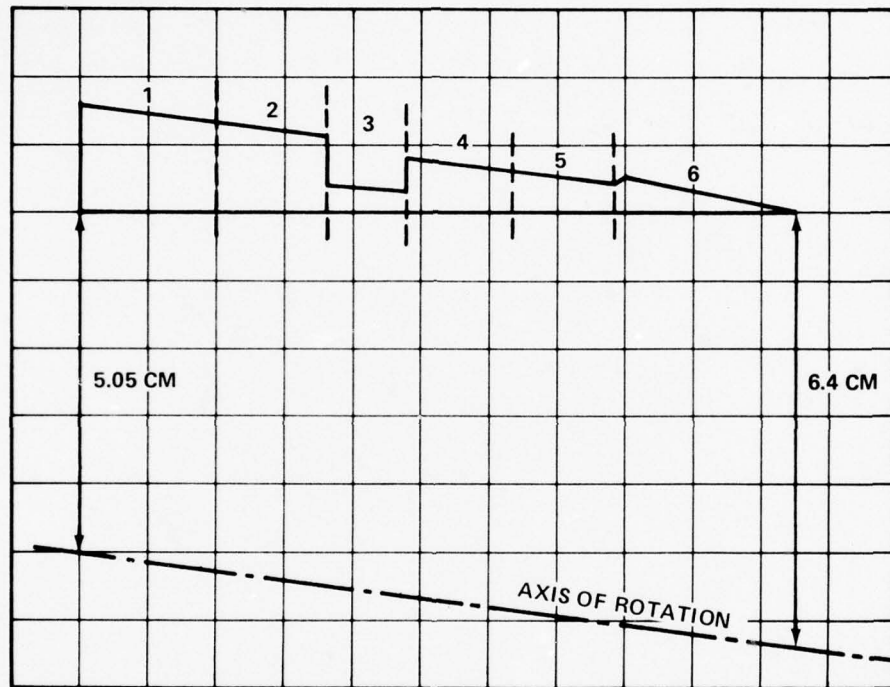
## ACKNOWLEDGEMENT

FIG. 1    CROSS SECTIONAL DIMENSIONS OF THE HIFRAG (5″/54)
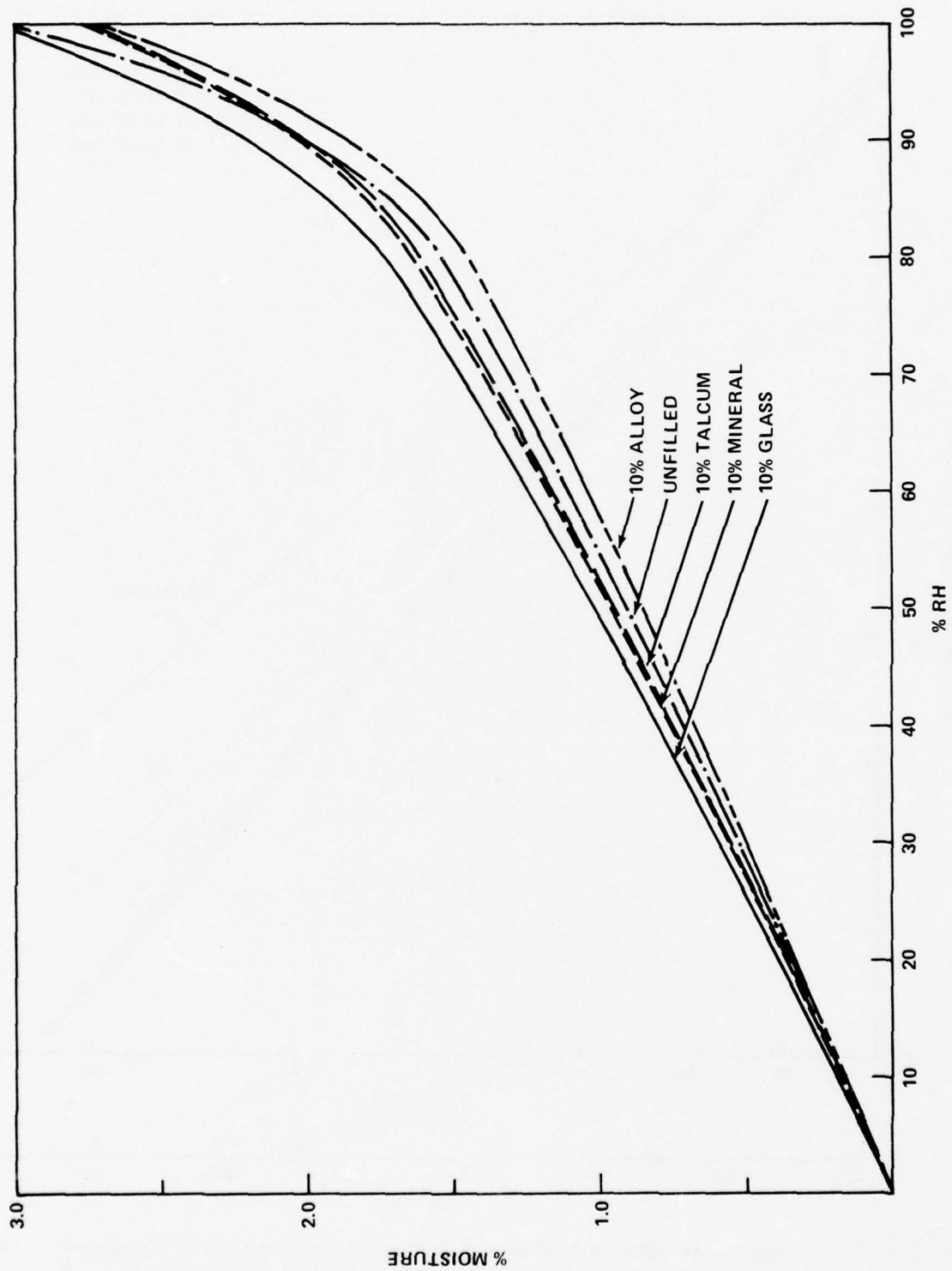DISCARDING ROTATING BAND.

FIG. 2   EQUILIBRIUM CONCENTRATIONS OF UNFILLED AND 10% FILLED NYLON 612.
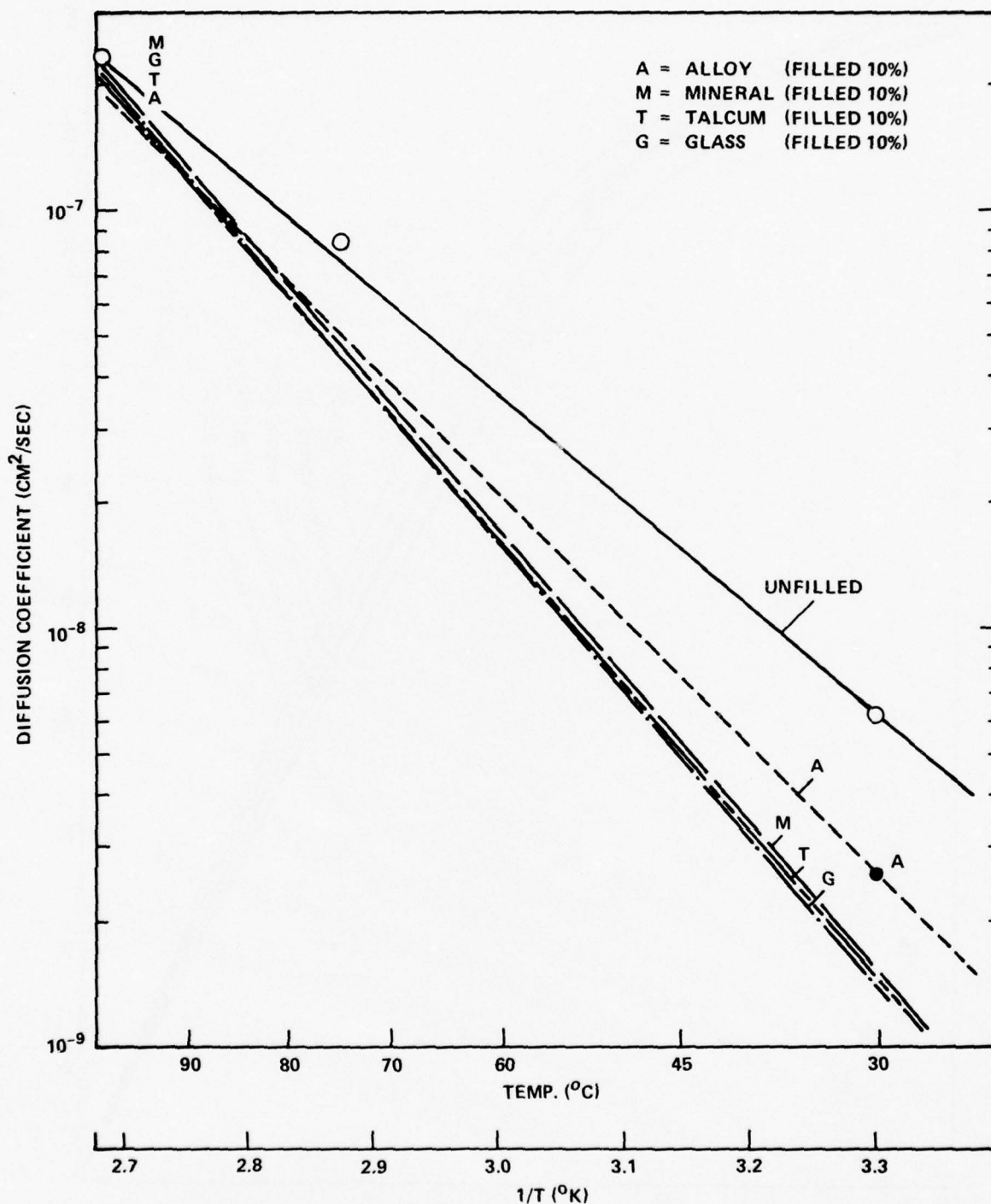
25

FIG. 3   ARRHENIUS PLOT OF THE DIFFUSION COEFFICIENTS OF NYLON 612
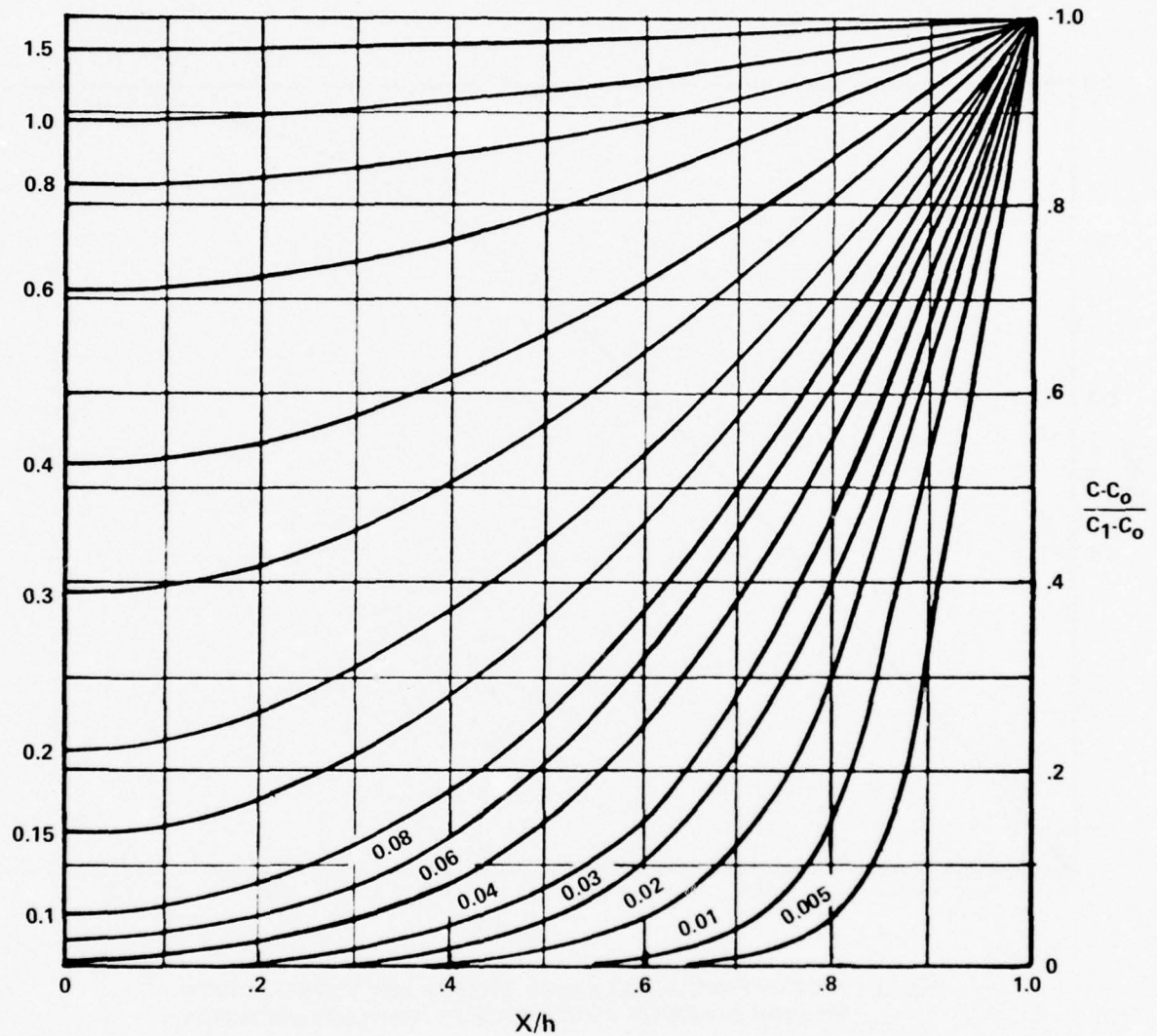(FILLED AND UNFILLED) AS A FUNCTION OF TEMPERATURE.

FIG. 4    CONCENTRATION DISTRIBUTION (MASTER PLOT) AT VARIOUS TIMES
IN THE SHEET $-h < X < h$ WITH INITIAL UNIFORM CONCENTRATION $C_0$
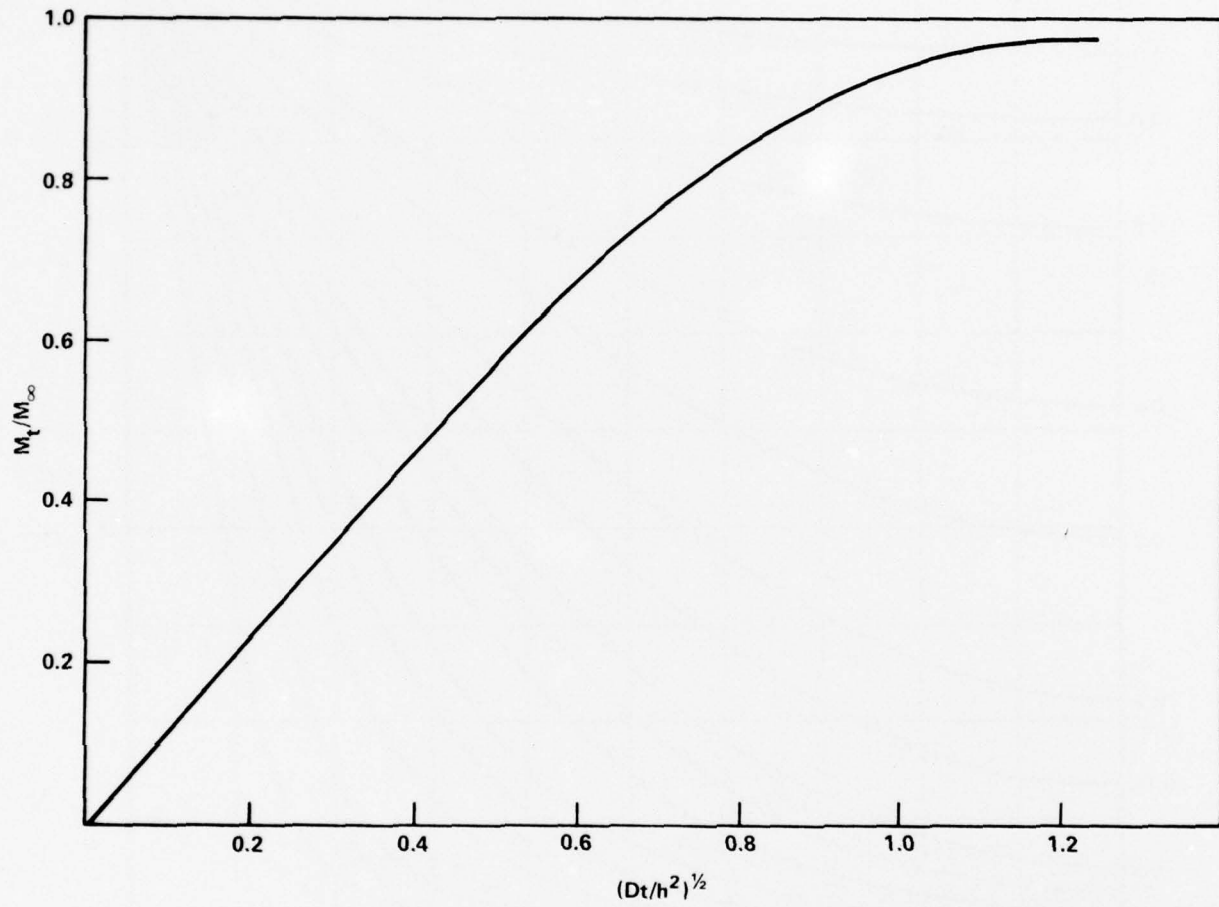AND SURFACE CONCENTRATION $C_1$. NUMBERS ON CURVES ARE
VALUES OF $Dt/h^2$.

FIG. 5   PLOT OF FRACTIONAL ABSORPTION OF ANY MATERIAL WITH
FICKEAN BEHAVIOR VERSUS $(Dt/h^2)^{1/2}$ FOR PLATE GEOMETRY.

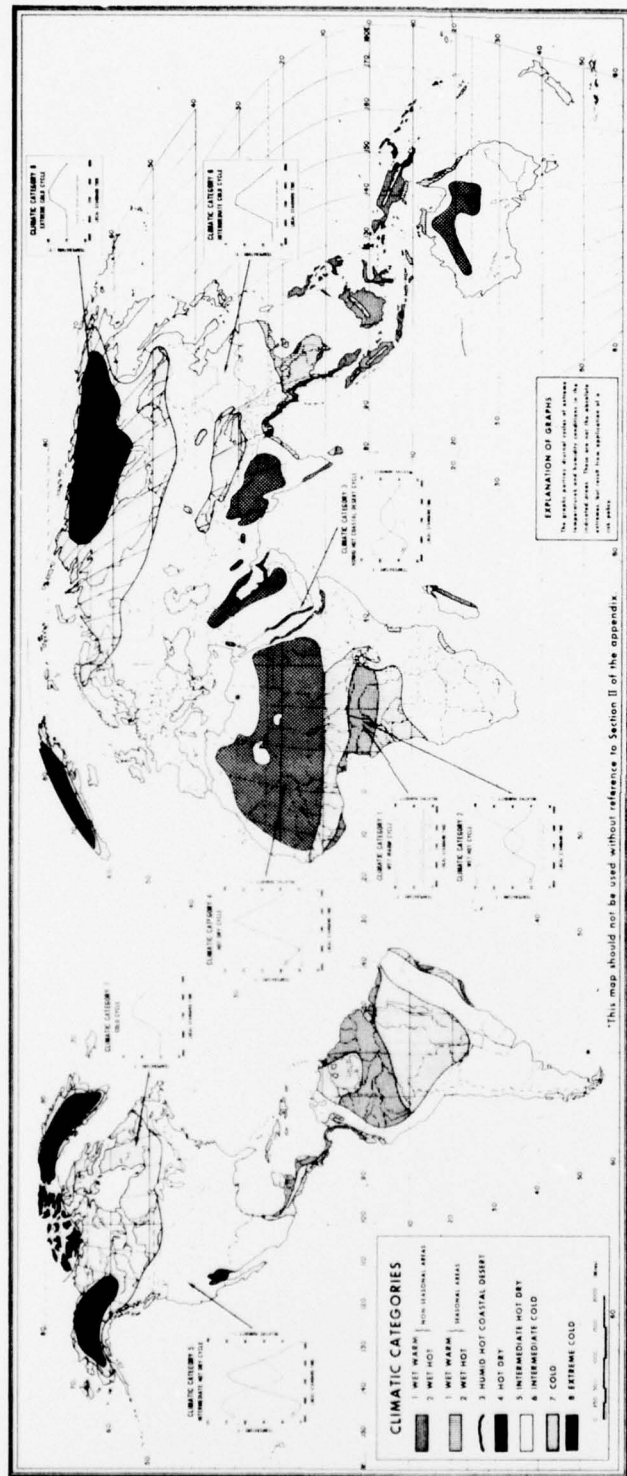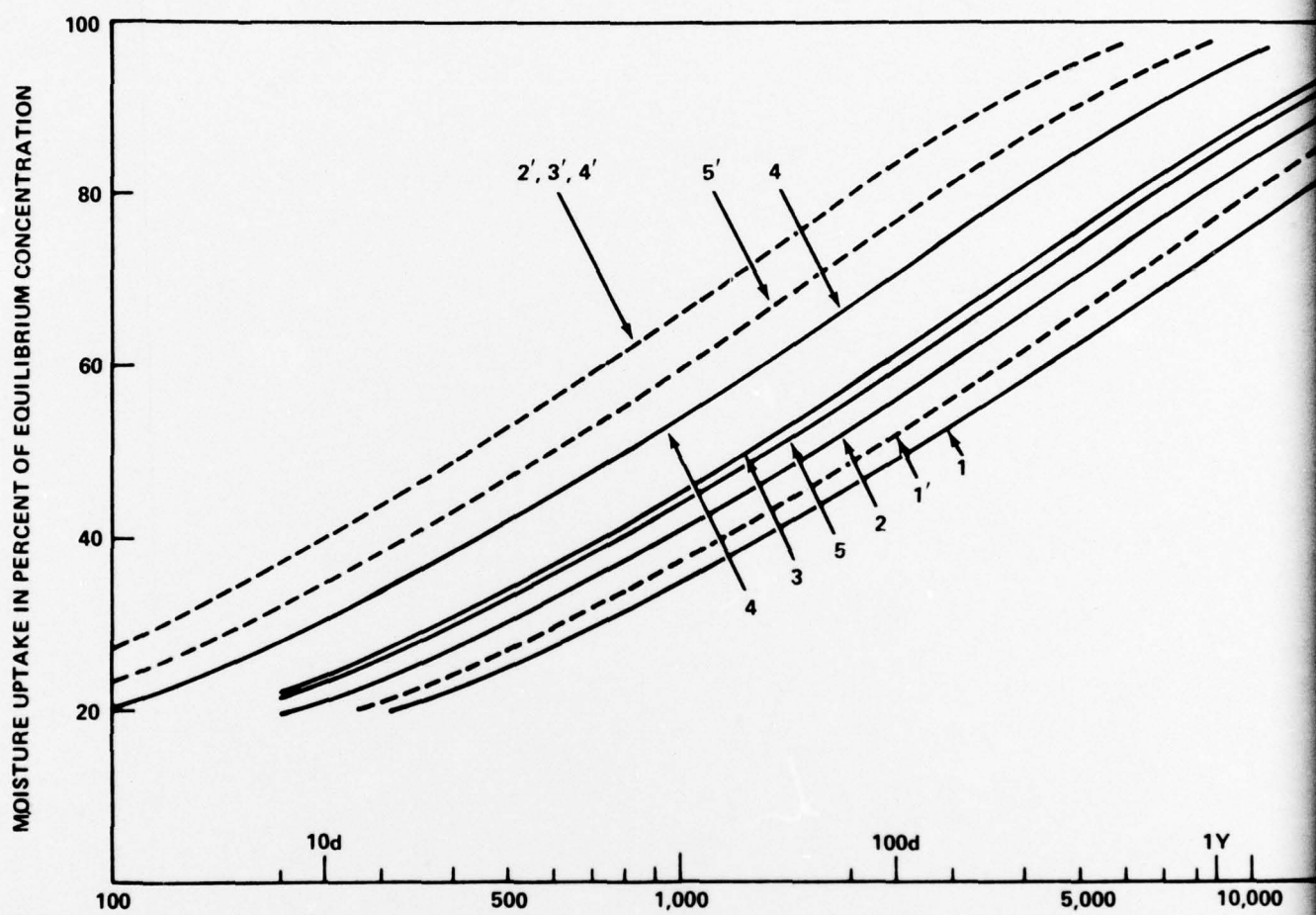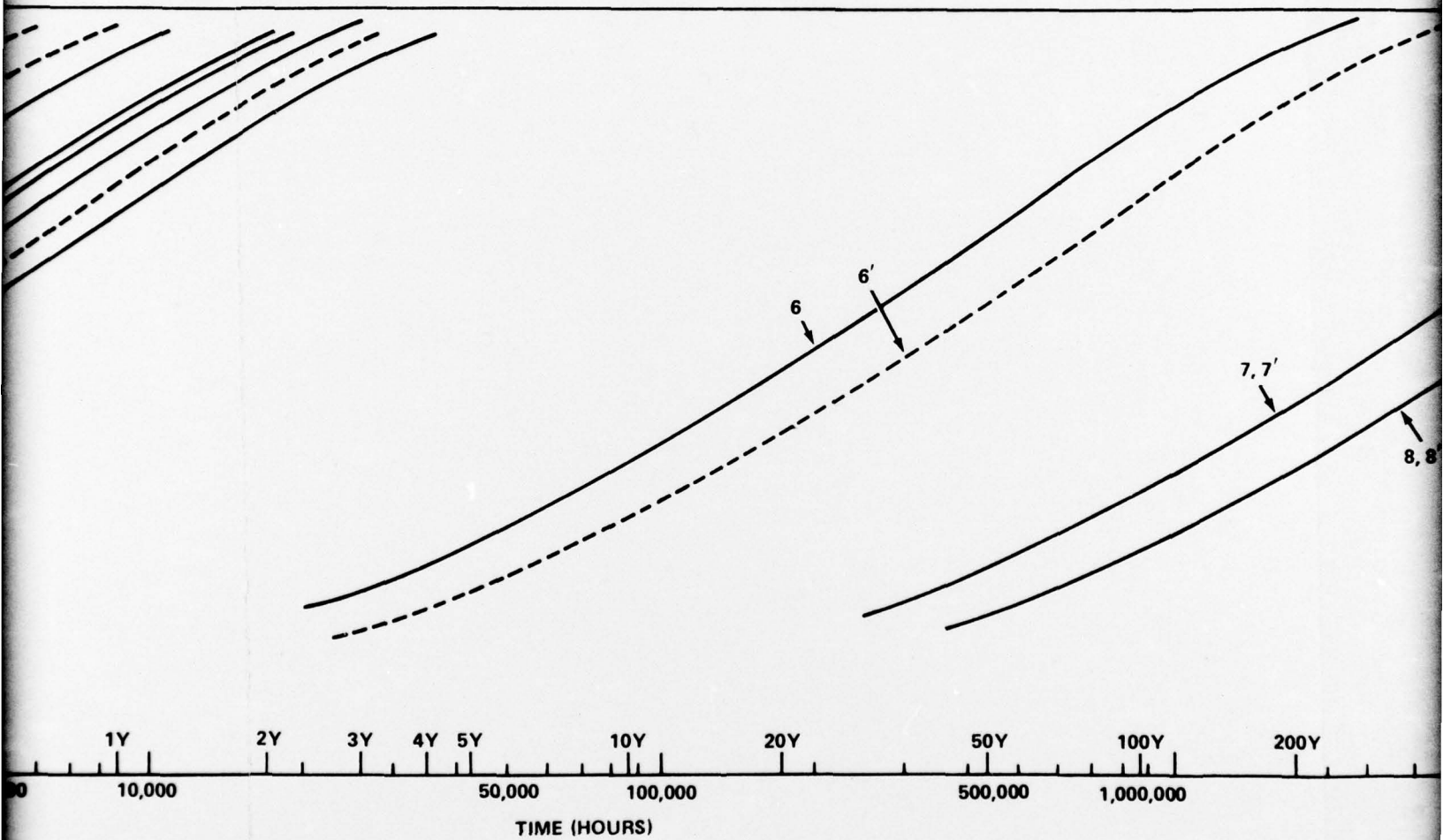**FIG. 6   AREAS OF OCCURRENCE OF CLIMATIC CATEGORIES.**

6    6'

7, 7'

8, 8'

1Y    2Y    3Y  4Y 5Y         10Y         20Y              50Y      100Y           200Y

10,000              50,000    100,000              500,000    1,000,000

TIME (HOURS)

FIG. 7   ABSOR

CLIMATIC CONDITIONS (AR 70-38)

| | OPERATIONAL | | | STORAGE | |
|---|---|---|---|---|---|
| CATEG. | °F | RH | | °F | RH |
| 1 | 75 | 97.5 | 1' | 80 | 97.5 |
| 2 | 86 | 88.5 | 2' | 120 | 55.9 |
| 3 | 93 | 73.4 | 3' | 120 | 55.9 |
| 4 | 105 | 11.5 | 4' | 120 | 28 |
| 5 | 88 | 55.5 | 5' | 106 | 28.6 |
| 6 | -16 | 100 | 6' | -24 | 100 |
| 7 | -43 | 100 | 7' | -43 | 100 |
| 8 | -66 | 100 | 8' | -66 | 100 |

7, 7'

8, 8'

50Y    100Y    200Y    500Y    1000Y

500,000    1,000,000    5,000,000    10,000,000
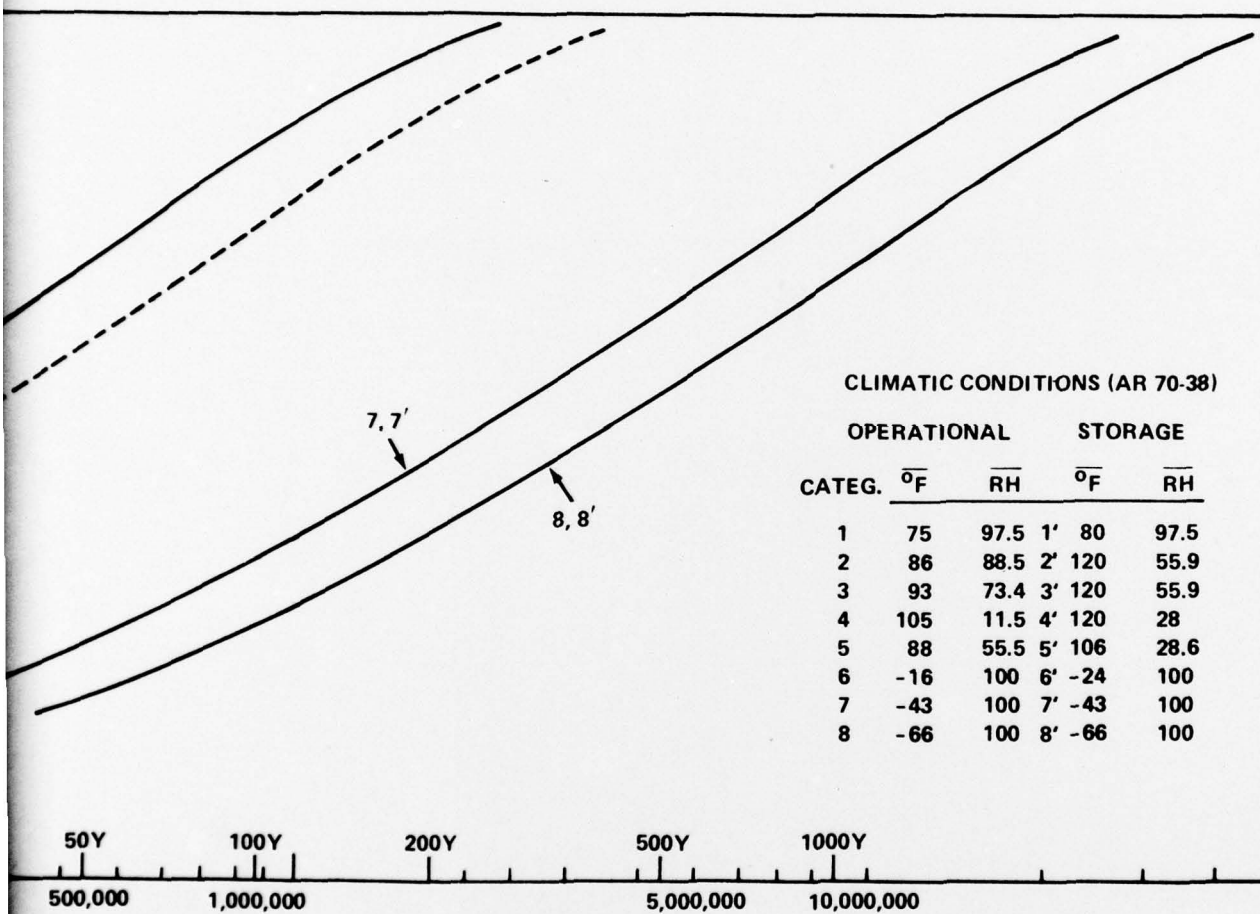
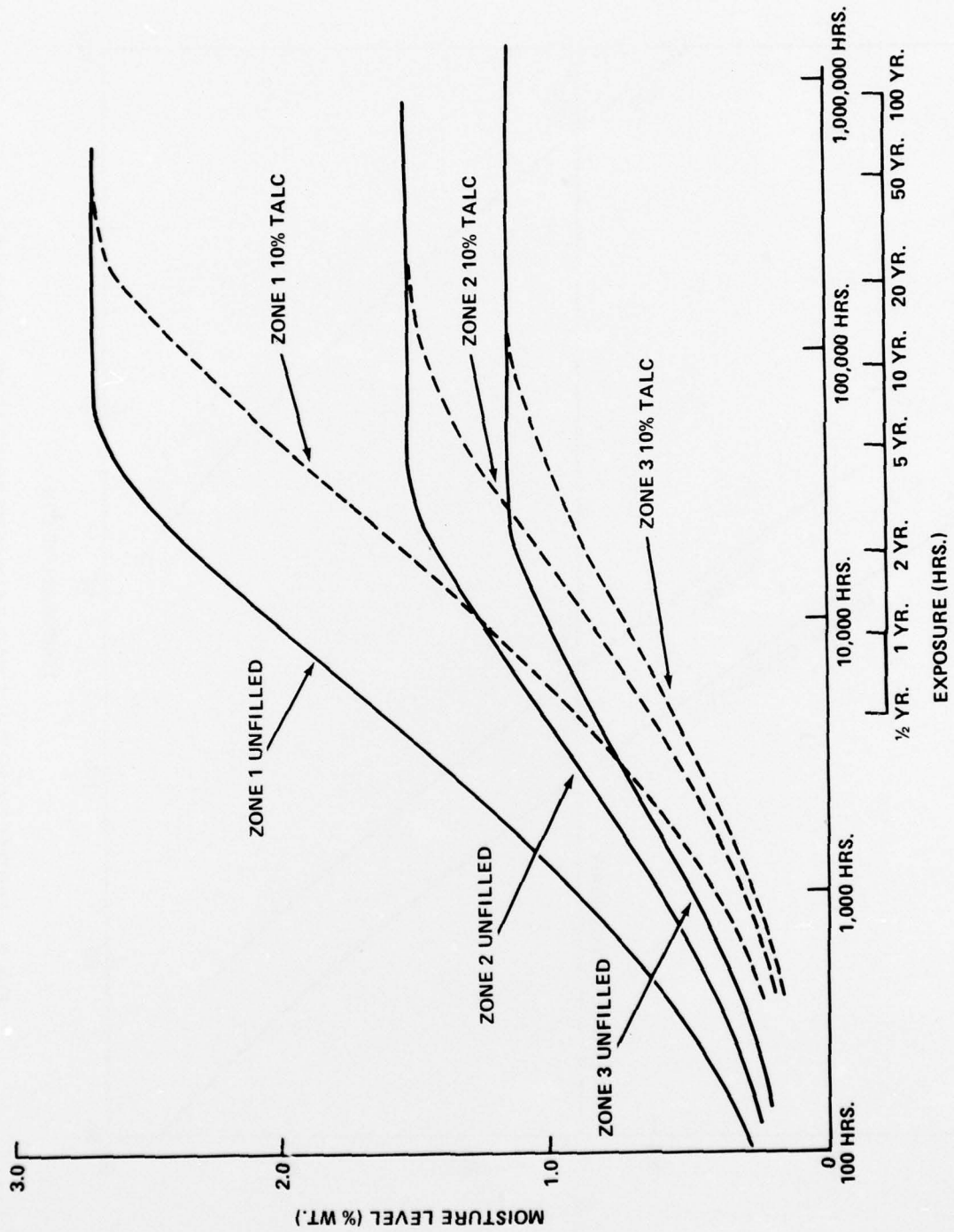FIG. 7    ABSORPTION OF MOISTURE IN (5"/54) ROTATING BAND.

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FIG. 8   ABSORPTION OF MOISTURE IN HIFRAG DRB IN AR 70-38 ENVIRONMENTS.

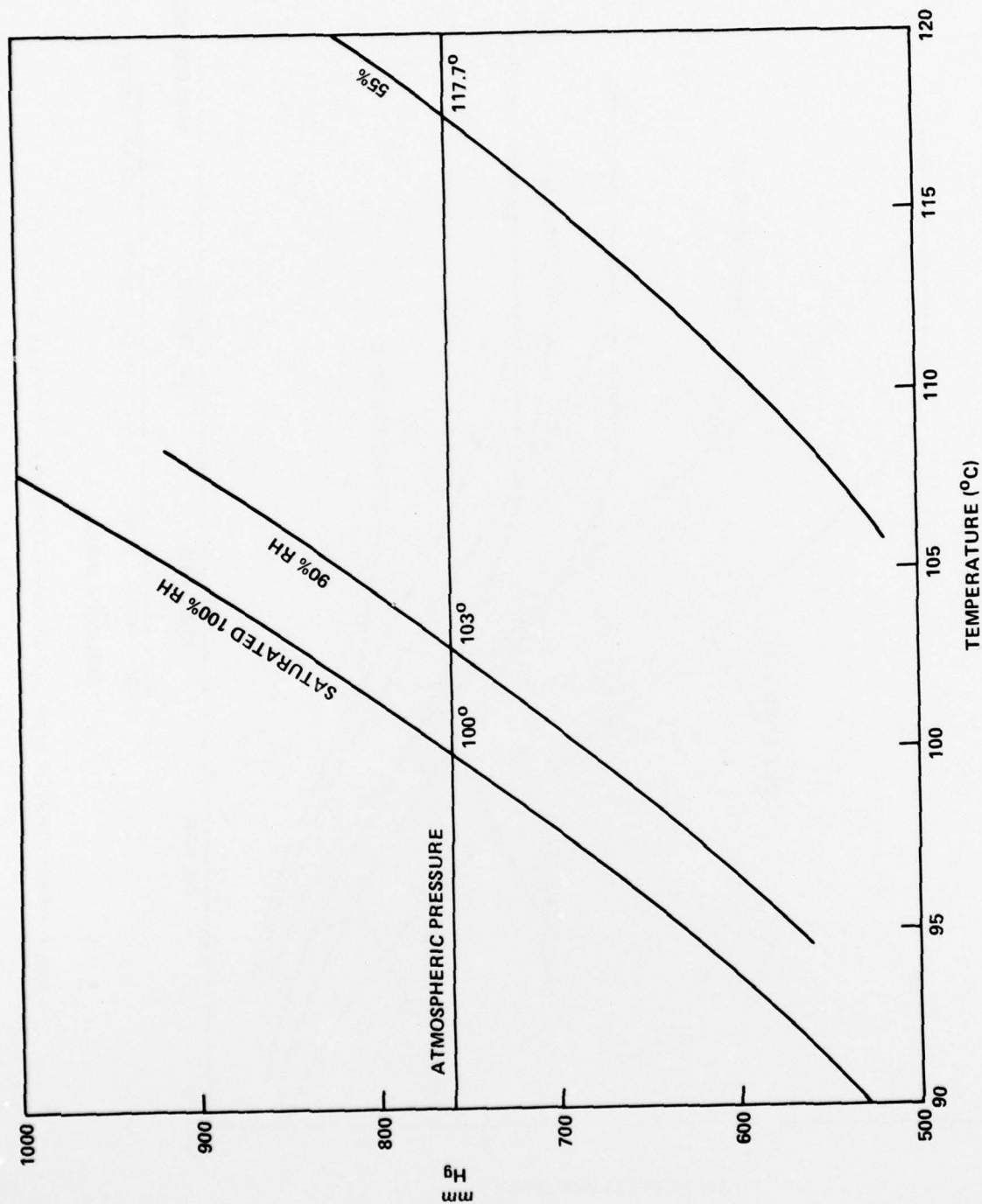FIG. 9    PARTIAL PRESSURE OF WATER CORRESPONDING TO 100, 90 AND 55% RH
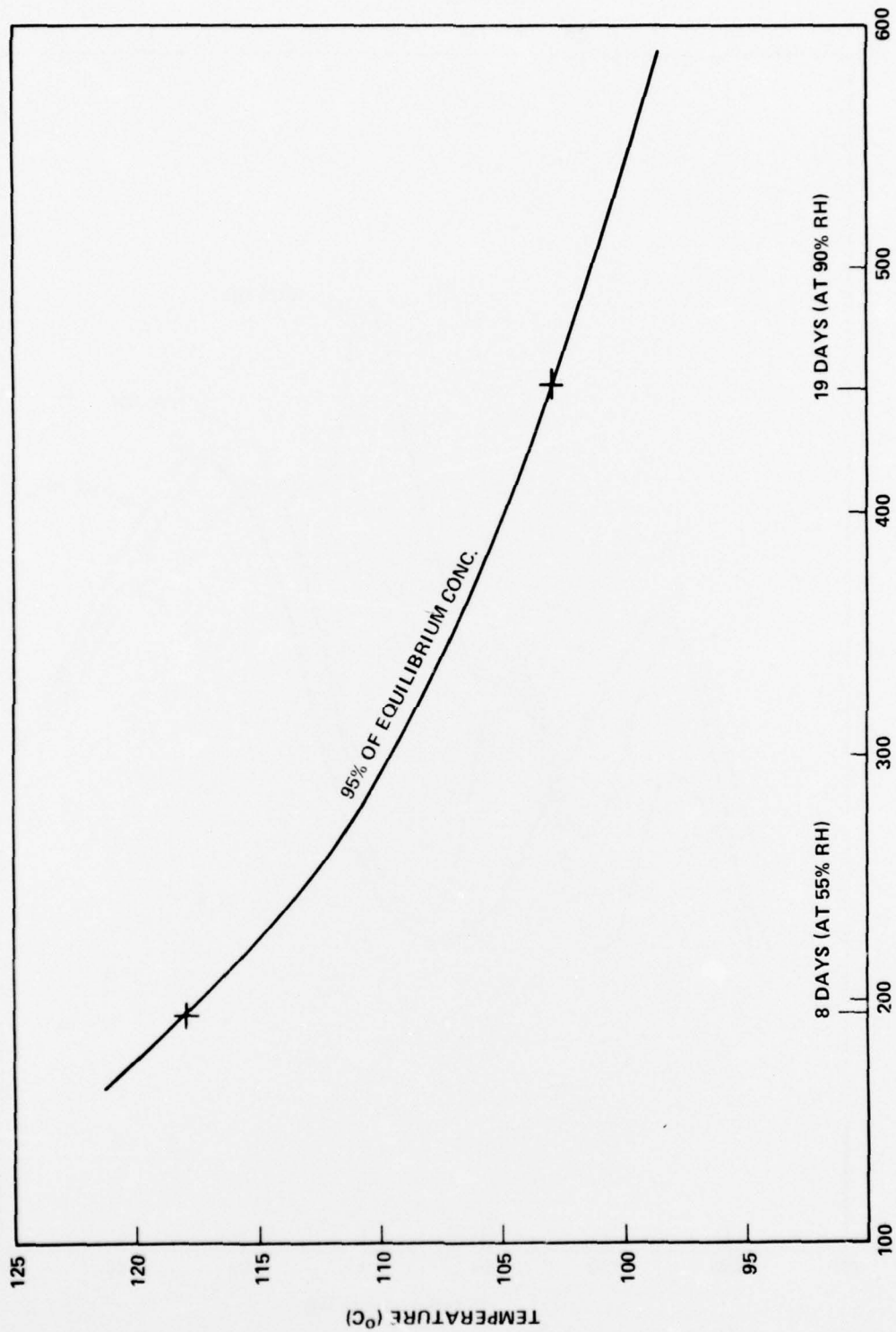AS A FUNCTION OF TEMPERATURE.

FIG. 10   TIME TO REACH 95% OF THE EQUILIBRIUM CONCENTRATION OF MOISTURE IN THE
5''/54 NYLON 612 ROTATING BAND AS A FUNCTION OF TEMPERATURE.
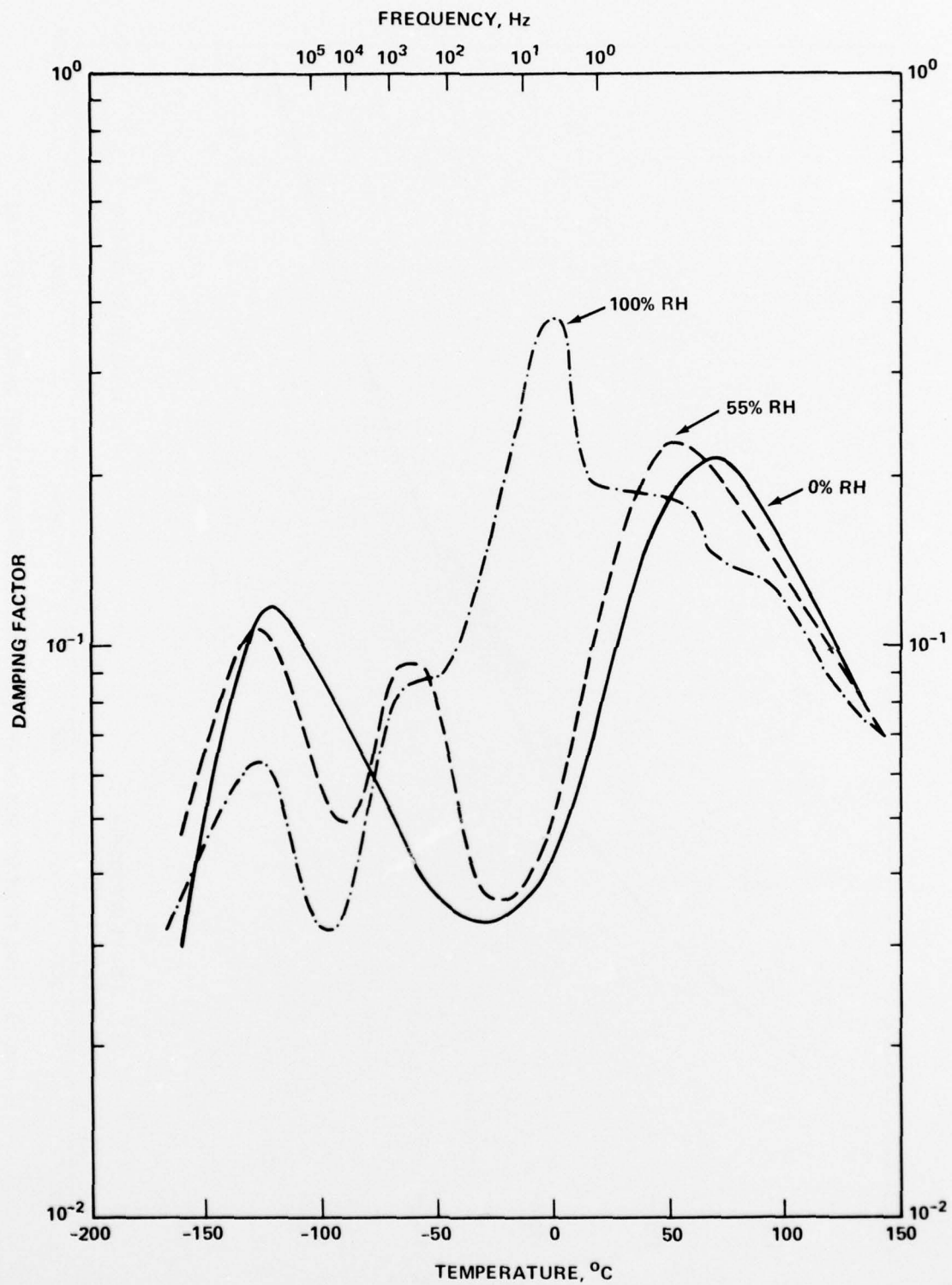
FIG. 11   DAMPING FACTOR VS. TEMPERATURE AND FREQUENCY
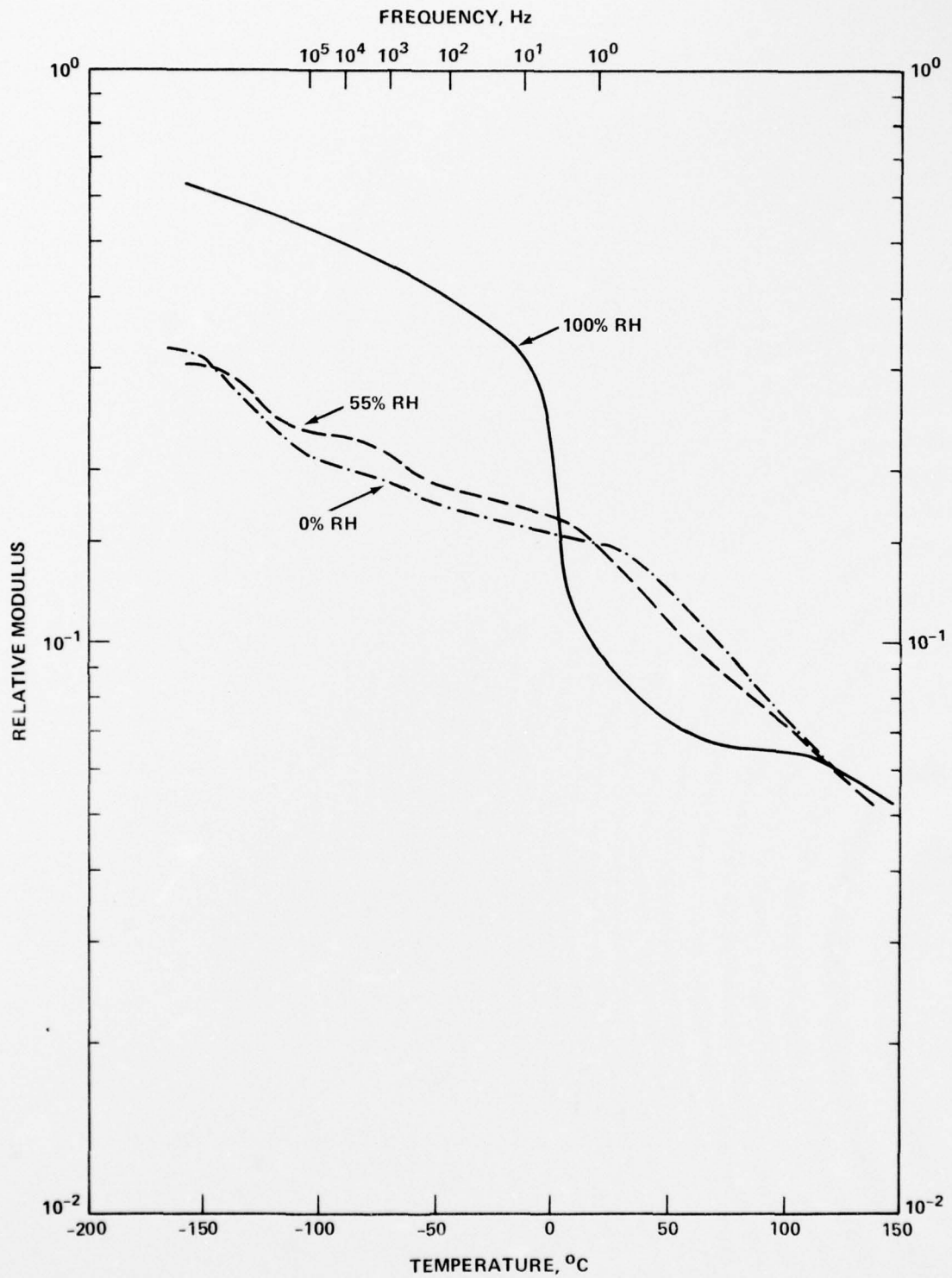AT 0, 55, AND 100% RH FOR NYLON 612.

FIG. 12   RELATIVE MODULUS VS. TEMPERATURE AND FREQUENCY
AT 0, 55, AND 100% RH FOR NYLON 612.

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